Surface Active Effect of Na_2O on the Rate of CO_2 Dissociation on the Surface of Molten $\text{FeO}_x\text{--Na}_2\text{O}$ and $\text{FeO}_x\text{--SiO}_2\text{--Na}_2\text{O}$ Systems

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It is well known that P_2O_5 and Na_2O have strong surface active effect in the molten oxide systems and affect the rate of oxidation or reduction of melts. In the previous work, the effect of P_2O_5 addition on the rate of CO_2 dissociation on the surface of FeO_x (FeO and Fe_2O_3)-based molten oxides was investigated by isotope exchange technique and it was confirmed that P_2O_5 strongly disturbs CO_2 dissociation. In the present study, the effect of Na_2O addition on the rate of CO_2 dissociation on the surface of $\text{FeO}_x\text{--Na}_2\text{O}$ and $\text{FeO}_x\text{--SiO}_2\text{--Na}_2\text{O}$ (mol% FeO_x :mol% SiO_2 =65:35) melts was measured at 1773 K with $P_{\text{CO}_2}/P_{\text{CO}}=1$ by isotope exchange technique. Reaction rate constant drastically increased with increasing Na_2O content for the $\text{FeO}_x\text{--Na}_2\text{O}$ system. On the other hand, rate constant gently increased for the $\text{FeO}_x\text{--SiO}_2\text{--Na}_2\text{O}$ system. The $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio of each system also slightly increased.

To estimate the rate constant from the composition of melts, the relationship between the rate constant and the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio for the $\text{FeO}_x\text{--CaO--SiO}_2$ system was also investigated. From the comparison of the estimated and observed rate constants, the strong promoting effect of Na_2O for CO_2 dissociation was confirmed in the $\text{FeO}_x\text{--Na}_2\text{O}$ system.

The surface active effect of Na_2O was analyzed by “smoothed surface potential model”, and the nature of molten oxide was discussed. From the obtained values, the surface tension of the molten oxide was estimated as a function of Na_2O concentration.

KEY WORDS: kinetics; reaction mechanism; isotope exchange technique; molten oxide; Na_2O ; surface active effect; smoothed surface potential model; surface tension.

1. Introduction

The reactions between CO--CO_2 gas and FeO_x -based molten oxides are quite important and the main phenomena in ironmaking and steelmaking processes. Therefore, oxidation or reduction rates for FeO_x -contained molten oxides have been widely investigated.^{1–13)} Researches about the reduction rate of FeO_x and FeO_x -based molten oxides with CO--CO_2 gas have been conducted by many researchers. Tsukihashi *et al.*²⁾ measured the reduction rate of molten iron oxide in CO gas conveyed system at 1723 and 1873 K. Fine powders of iron oxide were utilized to eliminate the effect of gas phase mass transfer rate on the overall reaction rate of reduction. Nagasaka *et al.*⁶⁾ also measured the reduction rate of molten iron oxide contained in an iron crucible under strong CO gas flow by using thermobalance in the temperature range of 1673 to 1723 K. Measured reduction rate constants were quite in good agreement with those measured by Tsukihashi *et al.* Meanwhile, the dissociation rates of CO_2 on the surface of molten oxides containing iron oxide have been measured by Sasaki *et al.*,³⁾ El-Rahaiby *et al.*,⁷⁾ Sun *et al.*⁸⁾ and Mori *et al.*¹¹⁾ with isotope exchange technique. If the dissociation of CO_2 is the rate determining step of oxidation of molten oxide, the reduc-

tion rate could be calculated from the measured dissociation rate constant. Belton¹⁴⁾ reported that there is very good accordance between the measured reduction rate and the dissociation rate. Therefore, the dissociation reaction of CO_2 is strongly expected as the rate determining step of the reaction between CO--CO_2 gas and molten oxide. Nagasaka *et al.*^{6,10)} estimated the dissociation rate constants of CO_2 from their measured reduction rate constant and those values were identical with measured values with isotope exchange technique.

Nagasaka *et al.*¹⁰⁾ also measured the effect of additives on the reduction rate of FeO_x -based molten oxide and it has been confirmed that the reaction rate constants are expressed as functions of temperature and compositions of ferrous and ferric iron in the molten oxides which represent thermodynamic state of melts. However, this expression could not be applied for molten oxides containing P_2O_5 or Na_2O due to their strong surface active effect.

The effect of Na_2O addition on the reaction rates has been investigated by Nagasaka *et al.*¹⁰⁾ and Sun and Belton.¹²⁾ Nagasaka *et al.* investigated the effect of Na_2O addition on the reduction rate of molten iron oxide with CO gas gravimetrically and the reduction rate constant increased 1.5 times by the approximately 4 mass% of Na_2O

addition. Sun and Belton measured the dissociation rate of CO_2 on the molten $\text{FeO}_x\text{-Na}_2\text{O}$ at 1 673 K with $\text{CO}_2/\text{CO}=5$ by $^{14}\text{CO}_2\text{-CO}$ isotope exchange technique, and they qualitatively confirmed the increase of dissociation rate constant by the small addition of Na_2O . However, the correct and quantitative analysis of the effect of Na_2O addition could not be conducted because of the inaccurate measured data due to the high volatility of Na_2O .

Therefore, available data are limited for the evaluation of the surface active effect of Na_2O on the reaction rate constant and for discussion of reaction mechanism. From this point of view, in the present study, the effect of Na_2O addition on the dissociation rate constant of CO_2 on the surface of the $\text{FeO}_x\text{-Na}_2\text{O}$ and the $\text{FeO}_x\text{-SiO}_2\text{-Na}_2\text{O}$ systems has been investigated by using $^{13}\text{CO}_2\text{-CO}$ isotope exchange technique¹⁵⁾ at 1 773 K to confirm the surface active effect of Na_2O and to clarify the applicability of surface covering model for the explanation of observed phenomena. The effect of Na_2O addition and the reaction mechanism were discussed based on the comparison with the effect of P_2O_5 addition previously investigated by present authors at 1 773 K.¹⁶⁾

2. Experimental

In the present study, CO-CO_2 gas containing $^{13}\text{CO}_2$ was utilized. Therefore, the isotope exchange reaction expressed as Eq. (1) occurs on the surface of molten oxide,

and the forward reaction rate constant of Eq. (1) is expressed as Eq. (2),¹⁴⁾

$$k = \frac{V}{ART} \frac{1}{B+1} \ln \frac{1 - P_{^{13}\text{CO}_2}^i / (P_{^{13}\text{CO}_2})_{\text{eq.}}}{1 - P_{^{13}\text{CO}_2}^o / (P_{^{13}\text{CO}_2})_{\text{eq.}}} \dots\dots\dots(2)$$

where, V is flow rate of reaction gas (m^3/s), A is the reaction area (m^2), R is gas constant ($\text{J/mol} \cdot \text{K}$), T is gas temperature (K) and $(P_{^{13}\text{CO}_2})_{\text{eq.}}$ is partial pressure of $^{13}\text{CO}_2$ under equilibrium of isotope exchange reaction. B is defined in Eq. (3),

$$\frac{P_{\text{CO}_2}}{P_{\text{CO}}} = \left(\frac{P_{^{13}\text{CO}_2}}{P_{^{13}\text{CO}}} \right)_{\text{eq.}} = B \dots\dots\dots(3)$$

The detail of experimental apparatus and procedures were essentially the same as reported in the previous paper.¹⁶⁾ About 5 g of premelted sample was put in a platinum crucible (I.D. 16 mm, O.D. 23 mm and height 18.5 mm), which has a thick bottom to supply sufficient heat, and that crucible and alumina tube (I.D. 16 mm, O.D. 21 mm and length 200 mm) were inserted in a transparent quartz tube (I.D. 45 mm, O.D. 50 mm and length 400 mm) which was set in an induction furnace. Sun and Belton¹²⁾ used about 0.5 g of slag films for their experiments, however Na_2O content of slag was drastically decreased due to the high volatility of Na_2O and correct measurements were inhibited. To avoid this problem, slag volumes used in the present study were increased to about 5 g and the effect of Na_2O content was successfully measured. As Na_2O content of slag decreased by volatilization, final Na_2O composition was determined by chemical analysis. Crucible and alumina tube were con-

nected carefully and tightly to prevent the reaction gas from contacting platinum which has high catalysis for isotope exchange reaction. Temperature was measured by dual wavelength pyrometer, which was calibrated by the temperature measurement of a platinum plate put in an electric furnace at 1 773 K.

FeO was prepared by melting a mixture of equimolar electrolytic iron and reagent grade Fe_3O_4 powder in an iron crucible at 1 723 K in argon atmosphere for 30 min before quenching on a steel plate. Prepared FeO , reagent grade of SiO_2 and Na_2CO_3 were preliminarily melted to prepare samples. The gas mixtures were prepared by mixing the high purity gases, which were passed through columns of H_2SO_4 , $\text{Mg}(\text{ClO}_4)_2$ and, for CO gas, soda lime for purification.

First, $\text{CO-}^{12}\text{CO}_2$ gas ($\text{CO}_2/\text{CO}=1$) was blown into a reaction tube through an alumina tube (I.D. 4 mm and O.D. 6 mm) held 8 mm above the surface of sample, and then crucible was heated to $1\,773 \pm 5$ K. The end position of the gas inlet tube was adjusted to the center of the crucible. Sample was held for at least 30 min to assure the equilibration with gas. Then, reaction gas was changed to $\text{CO-CO}_2\text{-Ar}$ gas containing about 2% of $^{13}\text{CO}_2$ with flow rate of approximately $5 \times 10^{-6} \text{ m}^3/\text{s}$ STP and isotope composition of outlet gas was continuously measured by quadrupole mass spectrometer (QMS). Confirming that the isotope gas composition of outlet gas became constant, isotope compositions of inlet and outlet gas were measured. After the each experiment, the oxide sample was quenched by splashing argon gas and analyzed by titration method with potassium dichromate for total iron and Fe^{2+} contents, ICP-AES for sodium content and gravimetry for SiO_2 content, respectively.

3. Results

Figure 1 shows an example of ion current profiles for each gas species measured by QMS. From these average ion currents of each species, $(P_{^{13}\text{CO}_2}/P_{^{12}\text{CO}_2})^i$ and $(P_{^{13}\text{CO}_2}/P_{^{12}\text{CO}_2})^o$ were calculated for the following calculation of reaction rate constant.

Experimental results and observed reaction rate constants at 1 773 K for the $\text{FeO}_x\text{-Na}_2\text{O}$ and the $\text{FeO}_x\text{-SiO}_2\text{-Na}_2\text{O}$

Fig. 1. Ion current profiles for each species measured by quadrupole mass spectrometer.

Table 1. Results of measured reaction rates and chemical analysis for each oxide system.

System	Exp. No.	$P(^{13}\text{CO}_2)^i$ (Pa)	$P(^{13}\text{CO}_2)^o$ (Pa)	$k_a \times 10^6$ (mol/m ² · s · Pa)	NaO _{0.5} content (mol%)	Fe ³⁺ /Fe ²⁺ ratio (-)
FeO _x -Na ₂ O	FN-1	753	653	3.681	0.00	0.177
	FN-2	857	743	3.372	0.00	0.192
	FN-3	803	659	5.178	0.83	0.215
	FN-4	772	599	6.711	2.08	0.199
	FN-5	765	592	7.542	2.42	0.192
	FN-6	861	645	8.147	3.59	0.225
	FN-7	774	535	11.457	7.45	0.238
	FN-8	756	510	13.343	9.74	0.259
	FN-9	751	519	14.060	12.84	0.249
	FN-10	685	509	14.889	15.82	0.280
FeO _x -SiO ₂ -Na ₂ O	FSN-1	820	800	0.543	0.00	0.130
	FSN-2	853	843	0.288	1.19	0.104
	FSN-3	859	847	0.339	2.67	0.073
	FSN-4	848	829	0.554	3.13	0.079
	FSN-5	849	829	0.569	6.65	0.109
	FSN-6	559	548	0.468	12.07	0.154
	FSN-7	772	752	0.631	12.78	0.135
	FSN-8	921	900	0.544	15.07	0.152
	FSN-9	845	811	0.989	16.92	0.125
	FSN-10	844	814	0.863	19.35	0.151
	FSN-11	838	803	1.022	21.71	0.128
	FSN-12	846	813	1.009	21.97	0.218

Fig. 2. Effect of Na₂O addition on the rate constant for the FeO_x-Na₂O system with $P_{\text{CO}_2}/P_{\text{CO}}=1$ at 1773 K. **Fig. 3.** Effect of Na₂O addition on the rate constant for the FeO_x-SiO₂-Na₂O system with $P_{\text{CO}_2}/P_{\text{CO}}=1$ at 1773 K.

(mol%FeO_x:mol%SiO₂=65:35) systems are shown in **Table 1** and in **Figs. 2** and **3**. The rate constant drastically increased with increasing Na₂O content in the FeO_x-Na₂O melt. On the other hand, the rate constant for the FeO_x-SiO₂-Na₂O melts gently increased. For both systems, the Fe³⁺/Fe²⁺ ratio was slightly increased with increasing Na₂O content as shown in **Fig. 4**. The effect of Na₂O addition on the Fe³⁺/Fe²⁺ ratio was expressed as a function of Na₂O content for both oxide systems as Eqs. (4) and (5),

(FeO_x-Na₂O system)

$$\text{Fe}^{3+}/\text{Fe}^{2+} = 0.549X_{\text{NaO}_{0.5}} + 0.193 \quad \text{.....(4)}$$

(FeO_x-SiO₂-Na₂O system)

$$\text{Fe}^{3+}/\text{Fe}^{2+} = 0.124X_{\text{NaO}_{0.5}} + 0.118 \quad \text{.....(5)}$$

In the case of experiments containing high concentration of Na₂O, the gas phase mass transfer might affect the measurements of reaction rate constants. Therefore, for FeO_x-Na₂O containing 12.8 mol% and 15.8 mol% NaO_{0.5} systems, the experiments were conducted with high gas flow rate, which is approximately twice (1×10^{-5} m³/s STP). Nevertheless, the measured results showed the same trend as the results with normal gas flow rate, that indicates, in the present experimental conditions, the effect of gas phase mass transfer is negligibly small even with the high reaction rate constants. From this finding, all results were analyzed with the assumption that measured reaction rate constants are equivalent to the interfacial reaction rate constants.

Nagasaka *et al.*⁽¹⁰⁾ investigated the effect of Na₂O addition on the reduction rate of FeO in FeO-Na₂O melts with

Fig. 4. Effect of Na_2O addition on the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio for the $\text{FeO}_x\text{-Na}_2\text{O}$ and the $\text{FeO}_x\text{-SiO}_2\text{-Na}_2\text{O}$ systems with $P_{\text{CO}_2}/P_{\text{CO}}=1$ at 1773 K.

Fig. 5. Relationship between the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio and the reaction rate constants for the $\text{FeO}_x\text{-CaO-SiO}_2$ system with $P_{\text{CO}_2}/P_{\text{CO}}=1$ at 1773 K.

CO gas at 1673 K by thermogravimetric method. Their results were converted into the rate constants at 1773 K by using the activation energy of 138 kJ/mol¹⁰⁾ and are plotted in Fig. 2, which also show the increase of rate constant by the addition on Na_2O . Larger increase with Na_2O addition was observed in the present experiments. Sun and Belton¹²⁾ measured the dissociation rate of CO_2 on the molten $\text{FeO}_x\text{-Na}_2\text{O}$ at 1673 K with $\text{CO}_2/\text{CO}=5$ and their measured data are also shown in Fig. 2. Their experiments were conducted for about 10 to 23 min to collect outlet gases for analyses of ^{14}CO content produced by the isotope exchange reaction. However, due to the high volatility of sodium oxide and the small slag amount of about 0.5 g, Na_2O content of slag was drastically decreased as mentioned above. Therefore, Na_2O content of samples were considered to change during experiments and the relationship between reaction rate constant and the Na_2O content could not be clearly derived.

To clarify the change of the reaction rate constant with the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio of molten oxides, some experiments were conducted for the $\text{FeO}_x\text{-CaO-SiO}_2$ system with $\text{CO}_2/\text{CO}=1$. Relationship between $\log(\text{Fe}^{3+}/\text{Fe}^{2+})$ and $\log k$

Fig. 6. Comparison of measured and estimated rate constants for the $\text{FeO}_x\text{-Na}_2\text{O}$ and the $\text{FeO}_x\text{-SiO}_2\text{-Na}_2\text{O}$ systems with $P_{\text{CO}_2}/P_{\text{CO}}=1$ at 1773 K.

is shown in Fig. 5 with the results observed in the previous paper.¹⁶⁾ It is known that the change of $\log(\text{Fe}^{3+}/\text{Fe}^{2+})$ by the change of CO_2/CO ratio shows the linear relationship with $\log k$ with a slope of -2 for pure FeO_x ,³⁾ $\text{FeO}_x\text{-SiO}_2$,⁷⁾ $\text{FeO}_x\text{-CaO}$,^{3,8)} and $\text{FeO}_x\text{-CaO-SiO}_2$ ⁷⁾ melts and these results indicate that two electrons play a key role for the dissociation of CO_2 on the melt. However, the change of $\text{Fe}^{3+}/\text{Fe}^{2+}$ was observed with changing CaO/SiO_2 ratio of slag system under constant CO_2/CO ratio in the present study. The reaction rate was increased by the increase of $\text{Fe}^{3+}/\text{Fe}^{2+}$ of melts. The dotted line measured by Sasaki *et al.*,³⁾ El-Rahaiby *et al.*⁷⁾ and Sun *et al.*⁸⁾ at 1793 K shows the same trend. From present results, change of reaction rate constant was expressed as a function of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio.

4. Discussion

4.1. Surface Active Effect of Na_2O on the Reaction Rate Constant

For both the $\text{FeO}_x\text{-Na}_2\text{O}$ and the $\text{FeO}_x\text{-SiO}_2\text{-Na}_2\text{O}$ systems, the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio was increased with increasing Na_2O content as expressed by Eqs. (4) and (5), respectively. Therefore, the change of the reaction rate constants with Na_2O addition could be estimated from the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio of melts by using Eqs. (4) and (5) with obtained relationship in Fig. 5. In Fig. 6, the dotted lines show the estimated reaction rate constants for both systems. For the $\text{FeO}_x\text{-Na}_2\text{O}$ system, a large difference between measured and estimated rate constants is observed, which is considered due to the surface active effect of Na_2O . Meanwhile, for the $\text{FeO}_x\text{-SiO}_2\text{-Na}_2\text{O}$ system, the measured and estimated constants are almost the same; this result indicates that Na_2O is not surface active for the $\text{FeO}_x\text{-SiO}_2\text{-Na}_2\text{O}$ system under the present condition. Na_2O has strong affinity with SiO_2 and the activity of Na_2O decreases with the increase of SiO_2 content in the silicate melts.¹⁷⁾ Therefore, it is considered that the segregation of Na_2O on the surface of melts is less activated for the $\text{FeO}_x\text{-SiO}_2\text{-Na}_2\text{O}$ system in comparison with the $\text{FeO}_x\text{-Na}_2\text{O}$ system because of the decrease of Na_2O activity.

4.2. Effect of Na₂O Addition on the Rate Constant and the Estimation of Surface Coverage

As mentioned above, Na₂O addition drastically increases the rate constant more than estimated from the change of the Fe³⁺/Fe²⁺ ratio of FeO_x-Na₂O melts. This phenomenon is considered as the surface active effect of Na₂O, which is known as drastic decrease of surface tension with the addition of Na₂O caused by the segregation of Na₂O for the FeO_x-Na₂O system as shown in Fig. 7.^{18,19)}

Comparing the effect of Na₂O addition with that of P₂O₅ reported in the previous paper,¹⁶⁾ the strong promoting effect of Na₂O is observed, which is different from the strong disturbing effect by P₂O₅ addition. The difference is considered to be originated with the affinity of Na₂O or P₂O₅ and CO₂ molecule. However, when the nature of molten oxides is considered, the affecting mechanism for CO₂ dissociation might be different between P₂O₅ and Na₂O addition, because the addition of Na₂O induces the increase of the Fe³⁺/Fe²⁺ ratio, while the addition of P₂O₅ does not affect. In the case of Na₂O addition, Na⁺ cations exist abundantly on the surface of melts and the local Fe³⁺/Fe²⁺ ratio becomes high, which causes the rapid increase of rate constant. In the case of P₂O₅ addition, PO₄³⁻ or their polymerized anions cover the surface of melts while the surface Fe³⁺/Fe²⁺ ratio keeps almost constant, which simply interfere the adsorption and/or the dissociation of CO₂ molecule.

Recently, Sun and Belton¹²⁾ proposed “smoothed surface potential model” for the surface active effect of P₂O₅ and Na₂O, which explains the effect of P₂O₅ or Na₂O addition on the rate constant as the change of local band gap between the conduction band and the valence band at the surface due to the change of surface potential with the addition of surfactants. Based on their model, the surface active effect of Na₂O is written as Eq. (6),

$$\ln \frac{k}{k_0} = - \frac{2F}{RT} \Delta \Phi_{\text{NaO}_{0.5}}^{\circ} \theta_{\text{NaO}_{0.5}} \dots \dots \dots (6)$$

where, k and k_0 are the rate constant when surface is covered with Na₂O of coverage $\theta_{\text{NaO}_{0.5}}$ and that with bare surface, respectively. F is Faraday constant. $\Delta \Phi_{\text{NaO}_{0.5}}^{\circ}$ is the change of surface potential when the surface is saturated with Na₂O. From above discussion, this model might be applicable to analyze the effect of Na₂O addition. To investigate the relationship between $\ln(k/k_0)$ and $\theta_{\text{NaO}_{0.5}}$, it is necessary to express the surface coverage with Na₂O as a function of Na₂O concentration. Applying the ideal Langmuir adsorption isotherm, surface coverage is expressed as a function of Na₂O content as Eq. (8),

$$\text{NaO}_{0.5}(\text{in slag}) + \boxed{\phantom{NaO_{0.5}}} = \boxed{\text{NaO}_{0.5}}(\text{ad}) \dots \dots \dots (7)$$

$$\theta_{\text{NaO}_{0.5}} = \frac{K_{\text{NaO}_{0.5}} a_{\text{NaO}_{0.5}}}{1 + K_{\text{NaO}_{0.5}} a_{\text{NaO}_{0.5}}} = \frac{K'_{\text{NaO}_{0.5}} X_{\text{NaO}_{0.5}}}{1 + K'_{\text{NaO}_{0.5}} X_{\text{NaO}_{0.5}}} \dots \dots \dots (8)$$

where, $K_{\text{NaO}_{0.5}}$, $a_{\text{NaO}_{0.5}}$ and $X_{\text{NaO}_{0.5}}$ are the adsorption coefficient of Eq. (7), activity and mole fraction of NaO_{0.5}, respectively. The standard state of activity is pure liquid of Na₂O. $K'_{\text{NaO}_{0.5}}$ is defined as $K'_{\text{NaO}_{0.5}} = K_{\text{NaO}_{0.5}} \times \gamma_{\text{NaO}_{0.5}}$. Therefore, by combining Eqs. (6) and (8), the following re-

Fig. 7. Surface tension measured with the “FeO”-Na₂O system.

Fig. 8. Relationship between $\ln(k/k_0)$ and mole fraction of NaO_{0.5} for the FeO_x-Na₂O system with $P_{\text{CO}_2}/P_{\text{CO}}=1$ at 1773 K.

lationship is deduced,

$$\ln \frac{k}{k_0} = - \frac{2F}{RT} \Delta \Phi_{\text{NaO}_{0.5}}^{\circ} \times \frac{K'_{\text{NaO}_{0.5}} X_{\text{NaO}_{0.5}}}{1 + K'_{\text{NaO}_{0.5}} X_{\text{NaO}_{0.5}}} \dots \dots \dots (9)$$

Figure 8 shows the relationship between $\ln(k/k_0)$ and $X_{\text{NaO}_{0.5}}$, and parameters were obtained by regression analysis of present measured data,

$$- \frac{2F}{RT} \Delta \Phi_{\text{NaO}_{0.5}}^{\circ} = 1.755 \pm 0.047, \quad K'_{\text{NaO}_{0.5}} = 29.0 \pm 2.3 \dots \dots \dots (10)$$

As shown in Fig. 8, the fitting curve shows extremely good agreement with present results.

From obtained $K'_{\text{NaO}_{0.5}}$, it is possible to estimate the surface tension of the FeO_x-Na₂O melt by the use of Langmuir-Szyszkowski equation, which was derived by Belton²⁰⁾ from the combination of Langmuir adsorption isotherm and Gibbs adsorption isotherm as Eq. (11),

$$\begin{aligned} \sigma &= \sigma^{\circ} - RT \Gamma_{\text{NaO}_{0.5}}^{\text{sat.}} \ln(1 + K_{\text{NaO}_{0.5}} a_{\text{NaO}_{0.5}}) \\ &= \sigma^{\circ} - RT \Gamma_{\text{NaO}_{0.5}}^{\text{sat.}} \ln(1 + K'_{\text{NaO}_{0.5}} X_{\text{NaO}_{0.5}}) \dots \dots \dots (11) \end{aligned}$$

Fig. 9. Estimated surface tension from present results at 1 773 K.

where, σ^0 and $\Gamma_{\text{NaO}_{0.5}}^{\text{sat}}$ are the surface tension of pure FeO_x and the saturating surface concentration of Na_2O , respectively. Surface tension of pure FeO_x was reported to be 590–600 mN/m by Kozakevitch.¹⁸⁾ However, unfortunately no literature data are available for the value of $\Gamma_{\text{NaO}_{0.5}}^{\text{sat}}$. Surface tension of the FeO_x – Na_2O system shown in Fig. 7 is expressed by Langmuir-Szyszkowski equation as Eq. (12),

$$\sigma (\text{mN/m}) = 594 - 85.7 \ln(1 + 52.9 X_{\text{NaO}_{0.5}}) \dots \dots \dots (12)$$

From this equation, $\Gamma_{\text{NaO}_{0.5}}^{\text{sat}}$ was calculated to be $6.16 \times 10^{-6} \text{ mol/m}^2$ at 1 673 K. Because $\Gamma_{\text{NaO}_{0.5}}^{\text{sat}}$ is unclear as a function of temperature, we assumed that $\Gamma_{\text{NaO}_{0.5}}^{\text{sat}}$ at 1 773 K is the same as the value at 1 673 K. Thereby, the surface tension of the FeO_x – Na_2O system equilibrated with CO – CO_2 gas ($\text{CO}_2/\text{CO}=1$) is expressed approximately as Eq. (13) at 1 773 K,

$$\sigma (\text{mN/m}) = 600 - 90.8 \ln(1 + 29.0 X_{\text{NaO}_{0.5}}) \dots \dots \dots (13)$$

Estimated surface tension of the FeO_x – Na_2O system was shown in Fig. 9. The estimated line is reasonable comparing with measured value shown in Fig. 9.

On the other hand, the change of surface potential when the surface is saturated with Na_2O could be estimated from Eq. (10) and the calculated value of $\Delta\Phi_{\text{NaO}_{0.5}}^0$ was -0.134 V . Considering dipole moment changes at the surface with the addition of Na_2O , the following equation is obtained,¹²⁾

$$\Delta m_{\text{NaO}_{0.5}} = \frac{\epsilon_0 \Delta\Phi_{\text{NaO}_{0.5}}^0}{N \Gamma_{\text{NaO}_{0.5}}^{\text{sat}}} \dots \dots \dots (14)$$

where, ϵ_0 and N are the permittivity of free space ($8.854 \times 10^{-12} \text{ F/m}$) and Avogadro's number, respectively. Therefore, from Eq. (14), the dipole moment per one Na atom $\Delta m_{\text{NaO}_{0.5}}$ could be calculated. The deduced value was $-3.20 \times 10^{-31} \text{ C} \cdot \text{m}$ or -0.0959 Debye . Comparing with -0.18 Debye reported by Sun and Belton,¹²⁾ the value of $\Delta m_{\text{NaO}_{0.5}} = -0.0959 \text{ Debye}$ is in good agreement with their deduced value within their large experimental error range due to the limited measured data, and the order of magnitude is, as they mentioned, physically reasonable with the obtained data of 0.103 Debye per one O atom on Pt(111) up to the coverage of $1 \times 10^{-5} \text{ mol/m}^2$ and of 0.62 Debye per atom on Pt(100) below $2 \times 10^{-6} \text{ mol/m}^2$ from the investigation of

work function change by the adsorption of oxygen on the surface of platinum by Derry and Ross.²¹⁾

5. Conclusions

The effect of Na_2O addition on the reaction rate of CO_2 dissociation on the surface of the FeO_x – Na_2O and the FeO_x – SiO_2 – Na_2O ($\text{mol}\% \text{FeO}_x : \text{mol}\% \text{SiO}_2 = 65 : 35$) was investigated by using isotope exchange technique at 1 773 K with $P_{\text{CO}_2}/P_{\text{CO}}=1$ atmosphere.

The rate constant drastically increased with increasing Na_2O content of the FeO_x – Na_2O melt. On the other hand, rate constant gently increased for the FeO_x – SiO_2 – Na_2O melts. For both systems, the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio was slightly increased with increasing Na_2O content.

The rate constants were estimated from the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio of molten oxides for both systems and the strong promoting effect of Na_2O was clarified for the FeO_x – Na_2O system, while the rate constants were almost the same as estimated for the FeO_x – SiO_2 – Na_2O system.

Rate constant of CO_2 dissociation for the FeO_x – Na_2O system was analyzed by “smoothed surface potential model” and the measured results were expressed by this model reasonably well. Based on the analyzed results, surface tension of FeO_x – Na_2O system equilibrated with CO – CO_2 gas ($\text{CO}_2/\text{CO}=1$) was estimated at 1 773 K.

From the relationship between the rate constant and the surface coverage of Na_2O , the change of surface potential when the surface is saturated with Na_2O , $\Delta\Phi_{\text{NaO}_{0.5}}^0$, was estimated as -0.134 V and the calculated dipole moment per one Na atom $\Delta m_{\text{NaO}_{0.5}}$ was -0.0959 Debye . This value was in good agreement with previously reported data, and also physically reasonable.

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